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MODIFICATION OF THE SULPHONATION TEST FOR CREOSOTE.

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MODIFICATION OF THE SULPHONATION TEST FOR CREOSOTE.

A NEW SULPHONATION TEST.[1]

The sulphonation test described in Forest Service Circular 112 has been found to give erratic results at different times and in the hands of different operators. The method was also rather long and tedious, making it altogether an unsatisfactory test. Since the publication of the method the conditions of the test have been made more specific, the time required has been shortened, the procedure has been made simpler, and the accuracy has been increased so as to give concordant reading in the hands of different operators. The significance of the test, described in Circular 112, is as follows:

> In contradistinction to the hydrocarbons of the paraffin series, those of the aromatic series react with concentrated sulphuric acid with marked ease. The products of this reaction, in which a sulpho group or groups replace hydrogen in the aromatic compound, are called sulphonic acids and the process is known as sulphonation. For example, the reaction with benzene would be $C_6H_6+H_2SO_4=C_6H_5SO_3H+H_2O$. The sulphonic acids are characterized by their solubility in water. If a fraction from the distillation of a creosote oil be treated under proper conditions with concentrated sulphuric acid, it will be converted into a mixture of sulphonic acids, which will readily dissolve in water. If, however, there are paraffin bodies present they will not be attacked to the same degree as the aromatic hydrocarbons, and when the products of the sulphonation are treated with water the paraffin components will remain as a residual oil. In applying this test to creosote oils it has been found that the most information is obtained by using it on the higher boiling fractions.

EXPERIMENTAL PART.

In a general way the sulphonation test may be divided into two stages: (1) The treating of the material with sulphuric acid, and (2) the separation of the unsulphonated residue from the reaction mixture. The first affects the accuracy of the test and the time required, while the second chiefly affects the time.

EXPERIMENTS WITH DIFFERENT STRENGTHS OF ACID.

Experiments were carried out with different strengths of acid, acting for different lengths of time. The strengths of acid used were ordinarily concentrated sulphuric (95 per cent H_2SO_4), 36 times normal sulphuric (96 per cent H_2SO_4), and 37, 38, and 39 times normal. With these different strength acids acting for different lengths of time the same numerical results were obtained under the following conditions:

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[1] The general method used in making this test is similar to that recommended in Bureau of Chemistry Bulletin 135 for the detection of mineral oils in turpentines, but several modifications have been made in order to obtain conditions more suitable for use with creosote.

1. 50 cc of ordinary acid reacting upon 10 cc of the creosote fraction for 17 hours at 98°.
2. 40 cc of 36 times normal acid acting upon 10 cc of creosote fraction for 3 hours at 98°.
3. 40 cc of 37 times normal acid acting upon 10 cc of creosote fraction for 1 hour at 98°.
4. 25 cc of 38 times normal acid acting upon 10 cc of creosote fraction without standing after the more vigorous reaction has ceased. (In all cases the acid was added to the creosote about 10 cc at a time, and the mixture was shaken for two minutes after each addition of acid.)

Of the four conditions the last is very difficult to control because of the extreme energy of the acid. This is shown by the fact that the temperature of the reaction mixture rose to over 100° C. within one minute after the addition of the acid to the creosote fraction. There is also a tendency of this acid to yield erratic results because the sulphonic acids formed by the reaction of the sulphuric acid on the creosote seem to include minute particles of unsulphonated oil, making it very difficult to effect a complete separation of the unsulphonated residue. The 39 times normal acid acted similarly to the 38 times normal, only the residue was even more difficult to separate. Of the first three methods the one best suited to the purpose of this test is the third, since it gives in the shortest time a residue which can be easily separated.

EXPERIMENTS WITH METHODS OF SEPARATING RESIDUE.

Experiments were carried out with different methods of separating the unsulphonated oils from the reaction mixture to determine if any difference could be obtained by using various methods of procedure. The three methods used were:

1. The reaction mixture after treatment was transferred to a separating funnel having a long graduated neck. The funnel was filled with acid and allowed to stand several hours until a constant reading of the volume of unsulphonated oil was obtained.
2. The reaction mixture after cooling was poured into a large volume of water. The unsulphonated oil which floated on the surface was collected and measured in a graduated cylinder.
3. The reaction was carried out in a Babcock milk bottle which after the completion of the reaction was cooled, filled to the top, and whirled in a Babcock centrifuge.

The readings on two oils treated in the same manner and with the same quantity of sulphuric acid, but with the sulphonation residue separated by different methods, are given in Table I.

TABLE I.—*Sulphonation residues obtained by different methods of separation.*

Sample—	Amount of unsulphonated oil.		
	Method No. 1.	Method No. 2.	Method No. 3.
	cc.	*cc.*	*cc.*
No. 1	0.9	0.9	0.88
No. 2	.6	.6	.61

In methods 1 and 2 the graduations in the measuring apparatus were in one-tenth of a cubic centimeter, while in method 3 they were in one two-hundredths of a cubic centimeter. This accounts for the slight difference shown in method 3. Of the three methods, No. 3 is the most rapid, since the reading can be determined within 15 minutes after the sulphuric acid has finished reacting, making the total test consume only 2 hours, as against from 7 to 17 in the other methods.

METHOD USED IN MAKING UP THE NORMAL ACIDS AND TESTING THEIR STRENGTH.

The ordinary concentrated sulphuric acid contains 95 per cent of acid, or between 35 and 36 times normal. Any acid stronger than this must be made by adding fuming sulphuric acid to the ordinary acid. Strong sulphuric acid and the fuming acid absorb moisture very rapidly from the air, and thus become diluted in a short time. In order to overcome this difficulty the following apparatus was used to weigh the acid for analysis: A small pipette similar to a medicine dropper was inserted in one hole of a two-holed rubber stopper and the other end of the hole plugged with a glass rod. In the other hole was inserted a glass rod bent at the upper end so that the whole arrangement could be hung on the arm of a balance. The weight of the apparatus was then found. In using the apparatus the pipette was removed from the stopper, filled with acid, quickly dried, put back into the stopper, and weighed. The whole apparatus was then carefully washed with water, the washings and acid diluted, titrated with standard alkali, and the result calculated for the strength of the acid in per cent of SO_3. The strengths of the ordinary concentrated acid and the fuming acid were determined in this way, and the percentage of each necessary to form the required mixture calculated. The calculation is a rather simple one, but for the sake of clearness an example is given below:

Percentage of SO_3 required in 37 times normal acid	80.07
Percentage of SO_3 found in the ordinary acid	77.38
Percentage of SO_3 found in the fuming acid	84.56

A unit of ordinary concentrated acid, therefore, contains too little SO_3 by (80.07—77.38) 2.69 per cent, and a unit of the fuming acid too much SO_3 by (84.56—80.07) 4.49 per cent. Consequently it is necessary to mix the two in the proportion of 269 parts of fuming acid (84.56 per cent SO_3) to 449 parts of ordinary concentrated acid (77.38 per cent SO_3) to obtain the 37 times normal acid having 80.07 per cent SO_3. It is always better to run a check analysis on the acid after mixing to make certain that the calculations were correct.

DESCRIPTION OF THE REVISED METHOD.

The revised or modified method finally adopted is as follows:

Ten cubic centimeters of the fraction of creosote to be tested are measured into a Babcock milk bottle. To this is added 40 cubic centimeters of 37 times normal acid, 10 cubic centimeters at a time. The bottle with its contents is shaken for two minutes after each addition of 10 cubic centimeters of acid. After all the acid has been added the bottle is kept at a constant temperature of from 98° to 100° C. for one hour, during which time it is shaken vigorously every 10 minutes. At the end of an hour the bottle is removed, cooled, and filled to the top of the graduation with ordinary sulphuric acid, and then whirled for five minutes in a Babcock separator. The unsulphonated residue is then read off from the graduations. The reading multiplied by 2 gives per cent by volume directly. (Each graduation equals one two-hundredths of a cubic centimeter.)

In well-equipped chemical laboratories the usual steam-jacket ovens, capable of maintaining a temperature of from 98° to 100° C., will keep the reaction mixture of the sulphuric acid and creosote at the proper temperature. It frequently happens, however, that creosotes are analyzed in a laboratory equipped only for that purpose, and for such cases a special steam bath or oven can be made by any tinsmith at small cost. It is essential that the chamber be of sufficient size to completely contain (under the cover) the Babcock bottle; otherwise the exact dimensions of the steam bath are unimportant, and any two vessels of suitable dimensions, which are at hand or can most readily be obtained, may be utilized in its construction. The accompanying figure illustrates the construction of a steam bath for this purpose.

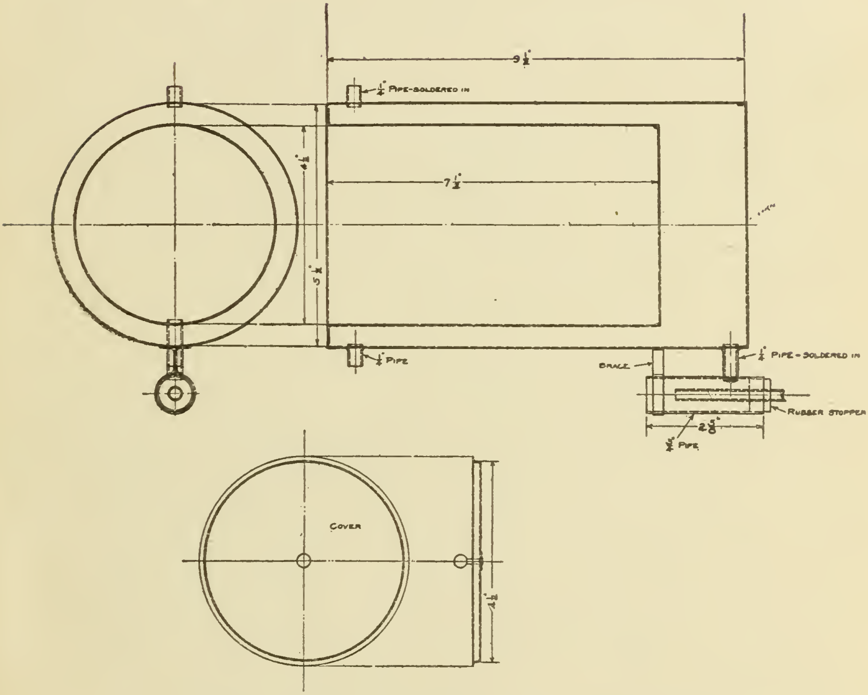

Fig. 1.—Steam bath for sulphonation test in creosote analysis.